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HYDROGELS COATED WITH STERIC OR ELECTROSTATIC SPACERS

Abstract:

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(54) HYDROGELS REVETUS DE SEPARATEURS STERIQUES OU ELECTROSTATIQUES
(54) HYDROGELS COATED WITH STERIC OR ELECTROSTATIC SPACERS

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(54) **Title:** HYDROGELS COATED WITH STERIC OR ELECTROSTATIC SPACERS

(54) **Bezeichnung:** HYDROGELE MIT STERISCHEN ODER ELEKTROSTATISCHEN ABSTANDHALTERN BESCHICHTET

(57) **Abstract:** The invention relates to non-water soluble hydrogels which can swell in water, and which are coated with steric or electrostatic spacers. Before being coated, the hydrogels comprise the following characteristics: absorbency under load (AUL) (0.7 psi) of at least 20 g/g, and gel strength of at least 1600 Pa. The coated hydrogels preferably have the following characteristics: centrifuge retention capacity (CRC) of at least 24 g/g, saline flow conductivity (SFC) of at least 30 x 10^{-7} cm^3 s/g, and free swell rate (FSR) of at least 0.15 g/g s and/or a maximum vortex time of 160 s.

(57) **Zusammenfassung:** Beschreiben werden nicht wasserlösliche wasserquellfähige Hydrogele, die mit sterischen oder elektrostatischen Abstandhaltern beschichtet sind, die vor dem Beschichten die folgenden Merkmale aufweisen: - Absorption unter Druck (AUL) (0,7 psi) von mindestens 20 g/g, Gelstärke von mindestens 1600 Pa, wobei die beschichteten Hydrogele vorzugsweise die folgenden Merkmale aufweisen: Zentrifugenretentionskapazität (CRC) von mindestens 24 g/g, Saline Flow Conductivity (SFC) von mindestens 30 x 10^{-7} cm^3 s/g und Free Swell Rate (FSR) von mindestens 0,15 g/g s und/oder Vortex Time von maximal 160 s.

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HYDROGELS COATED WITH STERIC OR ELECTROSTATIC SPACERS

This invention relates to hydrogels, to water-absorbent compositions containing same, to processes for their production, to their use in hygiene articles and to methods for determining suitable water-absorbent compositions.

Hygiene articles such as infant diapers or sanitary napkins have long been utilizing highly swellable hydrogels. This has substantially reduced hygiene article bulk.

The current trend in diaper design is toward even thinner constructions having a reduced cellulose fiber content and an increased hydrogel content. The advantage of thinner constructions shows itself not only in improved wear comfort, but also in reduced costs for packaging and warehousing. The trend toward ever thinner diaper constructions has substantially changed the profile of properties required of the water-swellable hydrophilic polymers. The decisive property is now the ability of the hydrogel to conduct and distribute imbibed fluid. The greater amount of polymer per unit area in the hygiene article must not cause the swollen polymer to form a barrier layer for subsequent fluid (gel blocking). Gel blocking occurs when fluid wets the surface of the highly absorbent hydrogel particles and the outer sheath swells. The result is the formation of a barrier layer which reduces diffusion of liquids into the particle interior and thus leads to leakage. Good gel permeability and thus good transportation properties ensures optimum utilization of the entire hygiene article.

The objective of higher use levels for highly swellable hydrogels has led through targeted adjustment of the degree of crosslinking in the starting polymer and subsequent postcrosslinking to an optimization of absorbency and gel strength. Improved gel permeability values can be generated only from a higher crosslink density in the starting polymer. Higher crosslink densities, however, go hand in hand with reduced absorption capacity and a decrease in the swell rate in the polymer. The consequence is that an increase in the hydrogel content of the hygiene article necessitates the incorporation of additional layers to prevent leakage, which in turn leads to bulky hygiene articles and is contrary to the actual objective of manufacturing thinner hygiene products.
A possible way to provide improved transportation properties and avoid gel blocking is to shift the particle size spectrum to higher values. However, this leads to a decrease in the swell rate, since the surface area of the absorbent material is reduced. This is undesirable.

Another way to obtain improved gel permeability is surface postcrosslinking, which confers higher gel strength on the hydrogel body in the swollen state. Gels having insufficient strength are deformable by pressure, for example pressure due to the bodyweight of the wearer of the hygiene article, and so clog the pores in the hydrogel/cellulose fiber absorbent and so prevent continued absorption of fluid. Since, for the above reasons, an increased crosslink density in the starting polymer is out of the question, surface postcrosslinking is an elegant way to increase gel strength. Surface postcrosslinking increases the crosslink density in the shell of the hydrogel particles, as a result of which Absorbency Under Load (AUL) by the base polymer thus generated is raised to a higher level. Whereas absorption capacity decreases in the hydrogel shell, the core of the hydrogel particles has an improved absorption capacity (compared to the shell) owing to the presence of mobile polymer chains, so that shell construction ensures improved fluid transmission.

However, high use levels of highly swellable hydrogels still give rise to the phenomenon of gel blocking. An important criterion must therefore be the ability to conduct fluid in the swollen state. Only good fluid conductance ensures full exploitations of the actual advantages of highly swellable hydrogels, namely their pronounced absorption and retention capacity for aqueous body fluids. However, it is important that fluid conductance take place in the intended use period of the hygiene article. And the full absorption capacity of the hydrogel should be utilized in the process. The ability of a hydrogel to conduct fluid is quantified in terms of the Saline Flow Conductivity (SFC). SFC measures the ability of the formed hydrogel layer to conduct fluid under a given pressure. It is believed that, at high use levels, hydrogel particles are in mutual contact in the swollen state to form a continuous absorption layer within which fluid distribution takes place.

A subsequent modification of the surface of the base polymers (surface-postcrosslinked starting polymers) is known.

DE-A-3 523 617 relates to the addition of finely divided amorphous silicas to dry hydrogel powder following surface postcrosslinking with carboxyl-reactive crosslinker substances.

In the prior art, aluminum sulfate is used as sole crosslinker or combined with other crosslinkers in surface postcrosslinking.

WO 95/22356 relates to the modification of absorbent polymers with other polymers to improve the absorption properties. Preferred modifiers are polyamines and polyimines. However, the effects with regard to SFC are minimal according to Tables 1 and 2.

WO 95/26209 relates to absorbent structures having at least one region containing 60-100% of highly swellable hydrogel having an SFC of at least 30×10^{-7} cm^3s/g and a PUP 0.7 psi of at least 23 g/g. It is exemplified that such highly swellable hydrogels are obtainable by surface postcrosslinking. As is evident from Tables 1 and 2, this type of treatment can provide an increased SFC only at the expense of a decreased gel volume, i.e., there is a reciprocal relationship between retention and gel permeability.

SFC increases with increasing particle size of the highly swellable hydrogel. As particle size increases, the surface area of the highly swellable hydrogel particles decreases relative to their volume, and this results in a decreased swell rate. It is therefore possible to deduce from the results of these experiments that swell rate too has a reciprocal dependency on SFC.

It is an object of the present invention to provide highly swellable hydrogels or water-absorbent compositions having good transportation properties and high permeability coupled with a high ultimate absorption capacity and a high swell rate when used in hygiene articles. Contrary to the prior art, where high absorption capacities on the part of the hydrogels, high liquid transportation performance and rapid swellability are mutually exclusive, the novel highly swellable hydrogels to be generated shall combine the contrary parameters. In addition, it shall be possible to produce thin hygiene articles through high use levels for the highly swellable hydrogels of the invention. Highly swellable hydrogels shall be generated for this purpose that simultaneously exhibit a high swell or absorption rate, a high gel permeability and a high retention. Given the excellent fluid distribution present, the high total capacity of the inventive highly swellable hydrogels in the absorption layer should be optimally utilizable.

We have found that this object is achieved according to the invention by water-insoluble water-swellable hydrogels coated with steric or electrostatic spacers, characterized by the following pre-coating features:

- Absorbency Under Load (AUL) (0.7 psi) of at least 20 g/g,

- Gel strength of at least 1 600 Pa.

The coated hydrogels additionally preferably have the following features:

- Centrifuge Retention Capacity (CRC) of at least 24 g/g,
- Saline Flow Conductivity (SFC) of at least 30×10^{-7}, preferably at least 60×10^{-7} cm^3s/g and
- Free Swell Rate (FSR) of at least 0.15 g/g and/or Vortex Time of not more than 160 s.

The term "water-absorbent" relates to water and aqueous systems which may contain organic or inorganic compounds in solution, especially to body fluids such as urine, blood or fluids containing same.

The hydrogels of the invention and water-absorbent compositions containing same are useful for producing hygiene articles or other articles for absorbing aqueous fluids. The invention consequently further relates to hygiene articles containing a water-absorbent composition according to the invention between a liquid-pervious topsheet and a liquid-impervious backsheet. The hygiene articles may be present in the form of diapers, sanitary napkins and incontinence products.

The invention also provides a method for improving the performance profile of water-absorbent compositions by enhancing the permeability, capacity and swell rate of the water-absorbent compositions by use of water-insoluble water-swellable hydrogels as defined above.

The invention further provides a method for determining water-absorbent compositions possessing high permeability, capacity and swell rate by measuring the absorbency under load (AUL) and the gel strength of uncoated hydrogels and determining the centrifuge retention capacity (CRC), Saline Flow Conductivity (SFC) and Free Swell Rate (FSR) of the coated hydrogels for given water-absorbent compositions and determining the water-absorbent compositions for which the hydrogels exhibit the property spectrum mentioned above.

The invention further provides for the use of hydrogels as defined above in hygiene articles or other articles for absorbing aqueous fluids to enhance the permeability, capacity and swell rate.

It was found that, surprisingly, the above object is achieved in full on using base polymers having an AUL (0.7 psi) of at least 20 g/g, preferably at least 22 g/g, particularly preferably at least 24 g/g, very preferably at least 26 g/g, and a gel strength of at least 1 600 Pa, preferably at least 1 800 Pa, particularly preferably at least 2 000 Pa, whose surface is subsequently coated with a steric (inert) or electrostatic spacer. Base polymers having these properties ensure that, under a restraining force, the spacer effect is not offset by excessively ready gel particle deformability.

The technique of adding steric or electrostatic spacers makes it possible to produce hygiene articles having a high hydrogel content within the absorption layer. In addition, hydrogels with electrostatic spacers also possess improved binding to cellulose fibers, since the latter have a weak negative charge on the surface. This fact is particularly advantageous, since it enables said property profile of hydrogels with electrostatic spacers and cellulose fibers to produce an absorption layer without additional assistants to fix the hydrogel within the fiber matrix. The binding to the cellulose fibers automatically effects fixation of the hydrogel material, so that there is no undesirable redistribution of the hydrogel material, for example to the surface of the absorbent core.

The highly swellable polymer particles of the invention are notable for high absorption capacities, improved liquid transportation performance and a higher swell rate. For this reason, the hygiene article can be made extremely thin. The increased level of high-capacity highly swellable hydrogels of the invention provides enormous absorption performance, so that the leakage problem is circumvented as well. At the same time, the improved liquid distribution performance ensures that the high absorption capacity is fully utilized.

The present invention relates to the production of novel highly swellable hydrogels by

(1) preselecting highly swellable base polymers having an AUL (0.7 psi) of at least 20 g/g, preferably at least 22 g/g, particularly preferably at least 24 g/g, very preferably at least 26 g/g, and a gel strength of at least 1 600 Pa, preferably at least 1 800 Pa, particularly preferably at least 2 000 Pa,

(2) aftertreating (coating) the surface of the base polymers selected according to the above criteria with steric or electrostatic spacers.

Coating these preselected hydrogels provides highly swellable hydrogels which, contrary to the prior art, combine a high swell or absorption rate with high gel permeability and a high retention.

This accordingly generates hydrogels having the following combinations of properties:

- CRC not less than 24 g/g, preferably not less than 26 g/g, more preferably not less than 28 g/g, even more preferably not less than 30 g/g, particularly preferably CRC not less than 32 g/g and most preferably CRC not less than 35 g/g

and

- SFC not less than 30 × 10^{-7} cm^3s/g, preferably not less than 60 × 10^{-7} cm^3s/g, preferably not less than 80 × 10^{-7} cm^3 s/g, more preferably not less than 100 × 10^{-7} cm^3 s/g, even more preferably not less than 120 × 10^{-7} cm^3 s/g, especially preferably not less than 150 × 10^{-7} cm^3 s/g, very preferably not less than 200 × 10^{-7} cm^3 s/g, most preferably not less than 300 × 10^{-7} cm^3 s/g,

and

- Free Swell Rate not less than 0.15 g/gs, preferably not less than 0.20 g/gs, more preferably not less than 0.30 g/gs, even more preferably not less than 0.50 g/gs, especially preferably not less than 0.70 g/gs, most preferably not less than 1.00 g/gs

  or

  Vortex Time not more than 160 s, preferably Vortex Time not more than 120 s, more preferably Vortex Time not more than 90 s, particularly preferably Vortex Time not more than 60 s, most preferably Vortex Time not more than 30 s.

Water-swellable hydrogels with spacers

Hydrogel-forming polymers are in particular polymers of (co)polymerized hydrophilic monomers, graft (co)polymers of one or more hydrophilic monomers on a suitable grafting base, crosslinked cellulose or starch ethers, crosslinked carboxymethylcellulose, partially crosslinked polyalkylene oxide or natural products that are swellable in aqueous fluids, for example guar derivatives, alginates and carrageenans.

Suitable grafting bases can be of natural or synthetic origin. Examples are starch, cellulose or cellulose derivatives and also other polysaccharides and oligosacchardies, polyvinyl alcohol, polyalkylene oxides, especially polyethylene oxides and polypropylene oxides, polyamines, polyamides and also hydrophilic polyesters. Suitable polyalkylene oxides have for example the formula

$$R^1-O-(CH_2-\underset{\displaystyle X}{\overset{}{CH}}-O)_n-R^2$$

where

R^1 and R^2 are independently hydrogen, alkyl, alkenyl or aryl,

X is hydrogen or methyl and

n is an integer from 1 to 10 000.

R^1 and R^2 are each preferably hydrogen, $(C_1$-$C_4)$-alkyl, $(C_2$-$C_6)$-alkenyl or phenyl.

Preferred hydrogel-forming polymers are crosslinked polymers having acid groups which are predominantly in the form of their salts, generally alkali metal or ammonium salts. Such polymers swell particularly strongly on contact with aqueous fluids to form gels.

Preference is given to polymers which are obtained by crosslinking polymerization or copolymerization of acid-functional monoethylenically unsaturated monomers or salts thereof. It is further possible to (co)polymerize these monomers without crosslinkers and to crosslink subsequently.

Examples of such monomers bearing acid groups are monoethylenically unsaturated C_3- to C_{25}-carboxylic acids or anhydrides such as acrylic acid, methacrylic acid, ethacrylic acid, α-chloroacrylic acid, crotonic acid, maleic acid, maleic anhydride, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid and fumaric acid. It is also possible to use monoethylenically unsaturated sulfonic or phosphonic acids, for example vinylsulfonic acid, allylsulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-acryloyloxypropylsulfonic acid, 2-hydroxy-3-methacryloyloxypropylsulfonic acid, vinylphosphonic acid, allylphosphonic acid, styrenesulfonic acid and 2-acrylamido-2-methylpropanesulfonic acid. The monomers may be used alone or mixed.

Preferred monomers are acrylic acid, methacrylic acid, vinylsulfonic acid, acrylamidopropanesulfonic acid or mixtures thereof, for example mixtures of acrylic and methacrylic acid, mixtures of acrylic acid and acrylamidopropanesulfonic acid or mixtures of acrylic acid and vinylsulfonic acid.

To optimize properties, it can be sensible to use additional monoethylenically unsaturated compounds which do not bear an acid group but are copolymerizable with the monomers bearing acid groups. Such compounds include for example the amides and nitriles of monoethylenically unsaturated carboxylic acids, for example acrylamide, methacrylamide and N-vinylformamide, N-vinylacetamide, N-methyl-N-vinylacetamide, acrylonitrile and methacrylonitrile. Examples of further suitable compounds are vinyl esters of saturated C_1- to C_4-carboxylic acids such as vinyl formate, vinyl acetate or vinyl propionate, alkyl vinyl ethers having at least 2 carbon atoms in the alkyl group, for example ethyl vinyl ether or butyl vinyl ether, esters of monoethylenically unsaturated C_3- to C_6-carboxylic acids, for example esters of monohydric C_1- to C_{18}-alcohols and acrylic acid, methacrylic acid or maleic acid, monoesters of maleic acid, for example methyl hydrogen maleate, N-vinyllactams such as N-vinylpyrrolidone or N-vinylcaprolactam, acrylic and methacrylic esters of alkoxylated monohydric saturated alcohols, for example of alcohols having from 10 to 25 carbon atoms which have been reacted with from 2 to 200 mol of ethylene oxide and/or propylene oxide per mole of alcohol, and also monoacrylic esters and monomethacrylic esters of polyethylene glycol or polypropylene glycol, the molar masses (M_n) of the polyalkylene glycols being up to 2 000, for example. Further suitable monomers are styrene and alkyl-substituted styrenes such as ethylstyrene or tert-butylstyrene.

These monomers without acid groups may also be used in mixture with other monomers, for example mixtures of vinyl acetate and 2-hydroxyethyl acrylate in any proportion. These monomers without acid groups are added to the reaction mixture in amounts within the range from 0 to 50% by weight, preferably less than 20% by weight.

Preference is given to crosslinked polymers of monoethylenically unsaturated monomers which bear acid groups and which are optionally converted into their alkali metal or ammonium salts before or after polymerization and 0-40% by weight, based on their total weight, of monoethylenically unsaturated monomers which do not bear acid groups.

Preference is given to crosslinked polymers of monoethylenically unsaturated C_3-C_{12}-carboxylic acids and/or their alkali metal or ammonium salts. Preference is given in particular to crosslinked polyacrylic acids, 25-100% of whose acid groups are present as alkali metal or ammonium salts.

Possible crosslinkers include compounds containing at least two ethylenically unsaturated double bonds. Examples of compounds of this type are N,N'-methylenebisacrylamide, polyethylene glycol diacrylates and polyethylene glycol dimethacrylates each derived from

polyethylene glycols having a molecular weight of from 106 to 8 500, preferably from 400 to 2 000, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, propylene glycol diacrylate, propylene glycol dimethacrylate, butanediol diacrylate, butanediol dimethacrylate, hexanediol diacrylate, hexanediol dimethacrylate, allyl methacrylate, diacrylates and dimethacrylates of block copolymers of ethylene oxide and propylene oxide, polyhydric alcohols, such as glycerol or pentaerythritol, doubly or more highly esterified with acrylic acid or methacrylic acid, triallylamine, dialkyldiallylammonium halides such as dimethyldiallylammonium chloride and diethyldiallylammonium chloride, tetraallylethylenediamine, divinylbenzene, diallyl phthalate, polyethylene glycol divinyl ethers of polyethylene glycols having a molecular weight of from 106 to 4 000, trimethylolpropane diallyl ether, butanediol divinyl ether, pentaerythritol triallyl ether, reaction products of 1 mol of ethylene glycol diglycidyl ether or polyethylene glycol diglycidyl ether with 2 mol of pentaerythritol triallyl ether or allyl alcohol, and/or divinylethyleneurea. Preference is given to using water-soluble crosslinkers, for example N,N'-methylenebisacrylamide, polyethylene glycol diacrylates and polyethylene glycol dimethacrylates derived from addition products of from 2 to 400 mol of ethylene oxide with 1 mol of a diol or polyol, vinyl ethers of addition products of from 2 to 400 mol of ethylene oxide with 1 mol of a diol or polyol, ethylene glycol diacrylate, ethylene glycol dimethacrylate or triacrylates and trimethacrylates of addition products of from 6 to 20 mol of ethylene oxide with 1 mol of glycerol, pentaerythritol triallyl ether and/or divinylurea.

Possible crosslinkers also include compounds containing at least one polymerizable ethylenically unsaturated group and at least one further functional group. The functional group of these crosslinkers has to be capable of reacting with the functional groups, essentially the acid groups, of the monomers. Suitable functional groups include for example hydroxyl, amino, epoxy and aziridino groups. Useful are for example hydroxyalkyl esters of the abovementioned monoethylenically unsaturated carboxylic acids, e.g., 2-hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate and hydroxybutyl methacrylate, allylpiperidinium bromide, N-vinylimidazoles, for example N-vinylimidazole, 1-vinyl-2-methylimidazole and N-vinylimidazolines such as N-vinylimidazoline, 1-vinyl-2-methylimidazoline, 1-vinyl-2-ethylimidazoline or 1-vinyl-2-propylimidazoline, which can be used in the form of the free bases, in quaternized form or as salt in the polymerization. It is also possible to use dialkylaminoalkyl acrylates and dialkylaminoalkyl methacrylates such as dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate and diethylaminoethyl methacrylate. The basic esters are preferably used in quaternized form or as salt. It is also possible to use glycidyl (meth)acrylate, for example.

Useful crosslinkers further include compounds containing at least two functional groups capable of reacting with the functional groups, essentially the acid groups, of the monomers. Suitable functional groups were already mentioned above, i.e., hydroxyl, amino, epoxy, isocyanate, ester, amido and aziridino groups. Examples of such crosslinkers are ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, polyglycerol, triethanolamine, propylene glycol, polypropylene glycol, block copolymers of ethylene oxide and propylene oxide, ethanolamine, sorbitan fatty acid esters, ethoxylated sorbitan fatty acid esters, trimethylolpropane, pentaerythritol, 1,3-butanediol, 1,4-butanediol, polyvinyl alcohol, sorbitol, starch, polyglycidyl ethers such as ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, glycerol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol polyglycidyl ether, pentaerythritol polyglycidyl ether, propylene glycol diglycidyl ether and polypropylene glycol diglycidyl ether, polyaziridine compounds such as 2,2-bishydroxymethylbutanol tris[3-(1-aziridinyl)propionate], 1,6-hexamethylenediethyleneurea, diphenylmethanebis-4,4'-N,N'-diethyleneurea, halo epoxy compounds such as epichlorohydrin and α-methyl-epifluorohydrin, polyisocyanates such as 2,4-toluylene diisocyanate and hexamethylene diisocyanate, alkylene carbonates such as 1,3-dioxolan-2-one and 4-methyl-1,3-dioxolan-2-one, also bisoxazolines and oxazolidones, polyamidoamines and also their reaction products with epichlorohydrin, also polyquaternary amines such as condensation products of dimethylamine with epichlorohydrin, homo- and copolymers of diallyl-dimethylammonium chloride and also homo- and copolymers of dimethylaminoethyl (meth)acrylate which are optionally quaternized with, for example, methyl chloride.

The crosslinkers are present in the reaction mixture for example from 0.001 to 20%, preferably from 0.01 to 14%, by weight.

The polymerization is initiated in the generally customary manner, by means of an initiator. But the polymerization may also be initiated by electron beams acting on the polymerizable aqueous mixture. However, the polymerization may also be initiated in the absence of initiators of the abovementioned kind, by the action of high energy radiation in the presence of photoinitiators. Useful polymerization initiators include all compounds which decompose into free radicals under the polymerization conditions, for example peroxides, hydroperoxides, hydrogen peroxides, persulfates, azo compounds and redox catalysts. The use of water-soluble initiators is preferred. In some cases it is advantageous to use mixtures of different polymerization initiators, for example mixtures of hydrogen peroxide and sodium peroxodisulfate or potassium peroxodisulfate. Mixtures of hydrogen peroxide and sodium peroxodisulfate may be used in any proportion. Examples of suitable

organic peroxides are acetylacetone peroxide, methyl ethyl ketone peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, tert-amyl perpivalate, tert-butyl perpivalate, tert-butyl perneohexanoate, tert-butyl perisobutyrate, tert-butyl per-2-ethylhexanoate, tert-butyl perisononanoate, tert-butyl permaleate, tert-butyl perbenzoate, di(2-ethylhexyl) peroxydicarbonate, dicyclohexyl peroxydicarbonate, di(4-tert-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate, diacetyl peroxydicarbonate, allyl peresters, cumyl peroxyneodecanoate, tert-butyl per-3,5,5-trimethylhexanoate, acetylcyclohexylsulfonyl peroxide, dilauryl peroxide, dibenzoyl peroxide and tert-amyl perneodecanoate. Particularly suitable polymerization initiators are water-soluble azo initiators, e.g., 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis-(N,N'-dimethylene)isobutyramidine dihydrochloride, 2-(carbamoylazo)isobutyronitrile, 2,2'-azobis[2-(2'-imidazolin-2-yl)propane] dihydrochloride and 4,4'-azobis(4-cyanovaleric acid). The polymerization initiators mentioned are used in customary amounts, for example in amounts of from 0.01 to 5%, preferably from 0.05 to 2.0%, by weight, based on the monomers to be polymerized.

Useful initiators also include redox catalysts. In redox catalysts, the oxidizing component is at least one of the above-specified per compounds and the reducing component is for example ascorbic acid, glucose, sorbose, ammonium or alkali metal bisulfite, sulfite, thiosulfate, hyposulfite, pyrosulfite or sulfide, or a metal salt, such as iron(II) ions or sodium hydroxymethylsulfoxylate. The reducing component in the redox catalyst is preferably ascorbic acid or sodium sulfite. Based on the amount of monomers used in the polymerization, from $3x10^{-6}$ to 1 mol% may be used for the reducing component of the redox catalyst system and from 0.001 to 5.0 mol% for the oxidizing component of the redox catalyst, for example.

When the polymerization is initiated using high energy radiation, the initiator used is customarily a photoinitiator. Photoinitiators include for example α-splitters, H-abstracting systems or else azides. Examples of such initiators are benzophenone derivatives such as Michler's ketone, phenanthrene derivatives, fluorene derivatives, anthraquinone derivatives, thioxanthone derivatives, coumarin derivatives, benzoin ethers and derivatives thereof, azo compounds such as the abovementioned free-radical formers, substituted hexaarylbisimidazoles or acylphosphine oxides. Examples of azides are:
2-(N,N-dimethylamino)ethyl 4-azidocinnamate, 2-(N,N-dimethylamino)ethyl 4-azidonaphthyl ketone, 2-(N,N-dimethylamino)ethyl 4-azidobenzoate, 5-azido-1-naphthyl 2'-(N,N-dimethylamino)ethyl sulfone, N-(4-sulfonylazido-phenyl)maleimide, N-acetyl-4-sulfonylazidoaniline, 4-sulfonylazidoaniline, 4-azidoaniline, 4-azidophenacyl bromide, p-azidobenzoic acid, 2,6-bis(p-azidobenzylidene)cyclohexanone and 2,6-bis(p-

azidobenzylidene)-4-methyl-cyclohexanone. Photoinitiators, if used, are customarily used in amounts of from 0.01 to 5% of the weight of the monomers to be polymerized.

The subsequent crosslinking stage comprises polymers which were prepared by polymerization of the abovementioned monoethylenically unsaturated acids and optionally monoethylenically unsaturated comonomers and which have a molecular weight of more than 5 000, preferably more than 50 000, being reacted with compounds having at least two groups which are reactive toward acid groups. This reaction can take place at room temperature or else at elevated temperatures of up to 220°C.

Suitable functional groups were already mentioned above, i.e., hydroxyl, amino, epoxy, isocyante, ester, amido and aziridino groups, as well examples of such crosslinkers. Crosslinkers are added to the acid-functional polymers or salts in amounts of from 0.5 to 25% by weight, preferably from 1 to 15% by weight, based on the amount of polymer used.

Crosslinked polymers are preferably used in fully neutralized form. However, neutralization may also be partial only. The degree of neutralization is preferably within the range from 25 to 100%, especially within the range from 50 to 100%. Useful neutralizing agents include alkali metal bases or ammonia/amines. Preference is given to the use of aqueous sodium hydroxide solution or aqueous potassium hydroxide solution. However, neutralization may also be effected using sodium carbonate, sodium bicarbonate, potassium carbonate or potassium bicarbonate or other carbonates or bicarbonates or ammonia. Moreover primary, secondary and tertiary amines may be used.

Industrial processes useful for making these products include all processes which are customarily used to make superabsorbents, as described for example in Chapter 3 of "Modern Superabsorbent Polymer Technology", F.L. Buchholz and A.T. Graham, Wiley-VCH, 1998.

Polymerization in aqueous solution is preferably conducted as a gel polymerization. It involves 10-70% strength by weight aqueous solutions of the monomers and optionally of a suitable grafting base being polymerized in the presence of a free-radical initiator by utilizing the Trommsdorff-Norrish effect.

The polymerization reaction may be carried out at from 0 to 150°C, preferably at from 10 to 100°C, not only at atmospheric pressure but also at superatmospheric or reduced

pressure. As is customary, the polymerization may also be conducted in a protective gas atmosphere, preferably under nitrogen.
By subsequently heating the polymer gels at from 50 to 130°C, preferably at from 70 to 100°C, for several hours, the performance characteristics of the polymers can be further improved.

Preference is given to hydrogel-forming polymers which have been surface postcrosslinked. Surface postcrosslinking may be carried out in a conventional manner using dried, ground and classified polymer particles.

To effect surface postcrosslinking, compounds capable of reacting with the functional groups of the polymers by crosslinking are applied to the surface of the hydrogel particles, preferably in the form of an aqueous solution. The aqueous solution may contain water-miscible organic solvents. Suitable solvents are alcohols such as methanol, ethanol, i-propanol or acetone.

Suitable surface postcrosslinkers include for example:

- di- or polyglycidyl compounds such as diglycidyl phosphonates or ethylene glycol diglycidyl ether, bischlorohydrin ethers of polyalkylene glycols,

- alkoxysilyl compounds,
  polyaziridines, aziridine compounds based on polyethers or substituted hydrocarbons, for example bis-N-aziridinomethane,

- polyols such as ethylene glycol, 1,2-propanediol, 1,4-butanediol, glycerol, methyltriglycol, polyethylene glycols having an average molecular weight M_w of 200 - 10 000, di- and polyglycerol, pentaerythritol, sorbitol, the ethoxylates of these polyols and their esters with carboxylic acids or carbonic acid such as ethylene carbonate or propylene carbonate,

- carbonic acid derivatives such as urea, thiourea, guanidine, dicyandiamide, 2-oxazolidinone and its derivatives, bisoxazoline, polyoxazolines, di- and polyisocyanates,

- di- and poly-N-methylol compounds such as, for example, methylenebis(N-methylolmethacrylamide) or melamine-formaldehyde resins,

- compounds having two or more blocked isocyanate groups such as, for example, trimethylhexamethylene diisocyanate blocked with 2,2,3,6-tetramethylpiperidin-4-one.

If necessary, acidic catalysts may be added, for example p-toluenesulfonic acid, phosphoric acid, boric acid or ammonium dihydrogenphosphate.

Particularly suitable surface postcrosslinkers are di- or polyglycidyl compounds such as ethylene glycol diglycidyl ether, the reaction products of polyamidoamines with epichlorohydrin and 2-oxazolidinone.

The crosslinker solution is preferably applied by spraying with a solution of the crosslinker in conventional reaction mixers or mixing and drying equipment such as Patterson-Kelly mixers, DRAIS turbulence mixers, Lödige mixers, screw mixers, plate mixers, fluidized bed mixers and Schugi Mix. The spraying of the crosslinker solution may be followed by a heat treatment step, preferably in a downstream dryer, at from 80 to 230°C, preferably 80-190°C, particularly preferably at from 100 to 160°C, for from 5 minutes to 6 hours, preferably from 10 minutes to 2 hours, particularly preferably from 10 minutes to 1 hour, during which not only cracking products but also solvent fractions can be removed. But the drying may also take place in the mixer itself, by heating the jacket or by blowing in a preheated carrier gas.

Steric spacers

Useful steric spacers include inert materials (powders) for example silicates having a band, chain or sheet structure (montmorillonite, kaolinite, talc), zeolites, active carbons or silicas. Inorganic inert spacers further include for example magnesium carbonate, calcium carbonate, barium sulfate, aluminum oxide, titanium dioxide and iron(II) oxide. Organic inert spacers include for example polyalkyl methacrylates or thermoplastics such as for example polyvinyl chloride. Preference is given to using silicas, which divide into precipitated silicas and pyrogenic silicas according to their method of preparation. Both variants are commercially available under the name AEROSIL® (pyrogenic silicas) or Silica FK, Sipernat®, Wessalon® (precipitated silica). The surface of the silica particles bears siloxane and silanol groups. There are more of the siloxane groups. They are the reason for the substantially inert character of this synthetic silica. Specific types of silica are available for different applications. For instance, silane may be added to chemically modify the silica surface so that the originally hydrophilic silica is transformed into hydrophobic variants. Some silica grades are available as mixed oxides, for example in a blend with aluminum oxide. The spacer function can be controlled according to the surface

constitution of the primary particles. Pyrogenic silica (for example AEROSIL®) is available in particle size fractions of from 7 to 40 nm.

Silica under the tradenames of Silica FK, Sipernat® and Wessalon® can be obtained as a powder of particle size fraction 5-100 μm and a specific surface area of 50-450 m^2/g.

For use as steric spacer, the particle size of the inert powders is preferably at least 1 μm, more preferably at least 4 μm, particularly preferably at least 20 μm, very preferably at least 50 μm. The use of precipitated silicas is particularly preferred.

The handling of inert silica grades is generally physiologically safe. This permits unreserved use of materials of this kind in a hygiene article.

The base polymers coated with inert spacer material may be produced by applying the inert spacers in an aqueous or water-miscible medium or else by applying the inert spacers in powder form to pulverulent base polymer material. The aqueous or water-miscible media are preferably applied by spraying onto dry polymer powder. In a particularly preferred version of the production process, pure powder/powder blends are produced from pulverulent inert spacer material and base polymer. The inert spacer material is applied to the surface of the base polymer in a proportion of 0.05 to 5% by weight, preferably from 0.1 to 1.5% by weight, particularly preferably from 0.3 to 1% by weight, based on the total weight of the coated hydrogel.

Electrostatic spacers

Cationic components may be added as electrostatic spacers.

It is generally possible to add cationic polymers for the purpose of electrostatic repulsion. This is accomplished for example with polyethyleneimines, polyvinylamines, polyamines such as polyalkylenepolyamines, cationic derivatives of polyacrylamides, polyethyleneimines, polyquaternary amines, for example, condensation products of hexamethylenediamine, dimethylamine and epichlorohydrin, condensation products of dimethylamine and epichlorohydrin, copolymers of hydroxyethylcellulose and diallyldimethylammonium chloride, copolymers of acrylamide and β-methacryloxyethyltrimethylammonium chloride, hydroxycellulose reacted with epichlorohydrin and then quaternized with trimethylamine, homopolymers of diallyldimethylammonium chloride or addition products of epichlorohydrin with amidoamines. Polyquaternary amines may further be synthesized by reaction of dimethyl sulfate with polymers, such as polyethyleneimines, copolymers of vinylpyrrolidone and dimethylaminoethyl methacrylate or copolymers of ethyl methacrylate and diethylaminoethyl methacrylate. Polyquaternary amines are available in a wide molecular weight range.

Electrostatic spacers are also generated by applying a crosslinked, cationic sheath, either by means of reagents capable of forming a network with themselves, for example addition products of epichlorohydrin with polyamidoamines, or by applying cationic polymers capable of reacting with an added crosslinker, for example polyamines or polyimines combined with polyepoxides, multifunctional esters, multifunctional acids or multifunctional (meth)acrylates. It is also possible to use any multifunctional amines having primary or secondary amino groups, for example polyethyleneimine, polyallylamine, polylysine, preferably polyvinylamine. Further examples of polyamines are ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylene-pentamine, pentaethylenehexamine and polyethyleneimines and also poly-amines having molar masses of up to 4 000 000 in each case.

Electrostatic spacers may also be applied by adding solutions of divalent or more highly valent metal salt solutions. Examples of divalent or more highly valent metal cations are Mg^{2+}, Ca^{2+}, Al^{3+}, Sc^{3+}, Ti^{4+}, Mn^{2+}, $Fe^{2+/3+}$, Co^{2+}, Ni^{2+}, $Cu^{+/2+}$, Zn^{2+}, Y^{3+}, Zr^{4+}, Ag^{+}, La^{3+}, Ce^{4+}, Hf^{4+} and $Au^{+/3+}$, preferred metal cations are Mg^{2+}, Ca^{2+}, Al^{3+}, Ti^{4+}, Zr^{4+} and La^{3+} and particularly preferred metal cations are Al^{3+}, Ti^{4+} and Zr^{4+}. The metal cations may be used not only alone but also mixed with each other. Of the metal cations mentioned, all salts are suitable that possess adequate solubility in the solvent to be used. Of particular suitability are metal salts with weakly complexing anions such as for example chloride, nitrate and sulfate. Useful solvents for the metal salts include water, alcohols, DMF, DMSO and also mixtures thereof. Particular preference is given to water and water-alcohol mixtures, for example water-methanol or water-1,2-propanediol.

In the production process, the electrostatic spacers may be applied like the inert spacers by application in an aqueous or water-miscible medium. This is the preferred production process in the case of the addition of metal salts. Cationic polymers are applied to pulverulent base polymer material by applying an aqueous solution or in a water-miscible solvent, optionally also as dispersion, or else by application in powder form. The aqueous or water-miscible media are preferably applied by spraying onto dry polymer powder. The polymer powder may optionally be subsequently dried, in which case the coated base polymers are exclusively dried at temperatures of not more than 100°C. Higher temperatures would lead to the formation of covalent bonds between the polyamine component and the polycarboxylate, which should be avoided under any circumstances in order that the additional crosslinking brought about as a result may not excessively lower the capacity of the product. For this reason, there is preferably no heat treatment step involved when coating with polyamines. When an additional crosslinker is used, the heat

treatment conditions are chosen in such a way that it is only the polyamine coating layer which is crosslinked, but not the polycarboxylate underneath.

The cationic spacers are applied to the surface of the base polymer in a proportion of from 0.05 to 5% by weight, preferably from 0.1 to 1.5% by weight, particularly preferably from 0.1 to 1% by weight, based on the total weight of the coated hydrogel.

The hydrogels mentioned are notable for high absorbency for water and aqueous solutions and therefore are preferentially used as absorbents in hygiene articles.

The water-swellable hydrogels may be present in conjunction with a box material for the hydrogels, preferably embedded as particles in a polymer fiber matrix or an open-celled polymer foam, fixed on a sheetlike base material or present as particles in chambers formed from a base material.

The invention also provides a process for producing water-absorbent compositions by

- preparing the water-swellable hydrogels,
- optionally coating the hydrogels with a steric or electrostatic spacer and
- introducing the hydrogels into a polymer fiber matrix or an open-celled polymer foam or into chambers formed from a base material or fixing on a sheetlike base material.

The hygiene articles producible from the water-absorbent compositions of the invention are known per se and have been described. They are preferably diapers, sanitary napkins and incontinence products such as incontinence liners. The construction of such products is known.

Description of test methods

Centrifuge Retention Capacity (CRC)

This method measures the free swellability of the hydrogel in a teabag. 0.2000 ± 0.0050 g of dried hydrogel (particle size fraction 106-850 μm) is sealed into a teabag 60 × 85 mm in size. The teabag is then soaked for 30 minutes in an excess of 0.9% by weight sodium chloride solution (at least 0.83 l of sodium chloride solution/1 g of polymer powder). The teabag is then centrifuged for three minutes at 250 g. The amount of liquid is determined by weighing the centrifuged teabag.

Absorbency Under Load (AUL) 0.7 psi

The measuring cell for determining AUL 0.7 psi is a Plexiglas cylinder 60 mm in internal diameter and 50 mm in height. Adhesively attached to its underside is a stainless steel sieve bottom having a mesh size of 36 µm. The measuring cell further includes a plastic plate having a diameter of 59 mm and a weight which can be placed in the measuring cell together with the plastic plate. The weight of the plastic plate and of the weight totals 1345 g. AUL 0.7 psi is determined by measuring the weight of the empty Plexiglas cylinder and of the plastic plate and recorded as W_0. 0.900 ± 0.005 g of hydrogel-forming polymer (particle size distribution: 150 - 800 µm) is then weighed into the Plexiglas cylinder and distributed very uniformly over the stainless steel sieve. The plastic plate is then carefully placed in the Plexiglas cylinder, the entire unit is weighed and the weight is recorded as W_a. The weight is then placed on the plastic plate in the Plexiglas cylinder. A ceramic filter plate 120 mm in diameter and 0 in porosity is then placed in the middle of a Petri dish 200 mm in diameter and 30 mm in height and sufficient 0.9% by weight sodium chloride solution is introduced for the surface of the liquid to be level with the filter plate surface without the surface of the filter plate being wetted. A round filter paper 90 mm in diameter and < 20 µm in pore size (S&S 589 Schwarzband from Schleicher & Schüll) is subsequently placed on the ceramic plate. The Plexiglas cylinder containing hydrogel-forming polymer is then placed with plastic plate and weight on top of the filter paper and left there for 60 minutes. At the end of this period, the complete unit is removed from the filter paper in the Petri dish and subsequently the weight is removed from the Plexiglas cylinder. The Plexiglas cylinder containing swollen hydrogel is weighed together with the plastic plate and the weight recorded as W_b.

AUL is calculated by the following equation:

$$\text{AUL 0.7 psi [g/g]} = [W_b - W_a] / [W_a - W_0]$$

Free Swell Rate (FSR)

1.00 g (W_H) of hydrogel is uniformly spread out on the bottom of a plastic weighing boat having a round bottom of about 6 cm. The plastic weighing boat is round and about 6 cm in diameter at the bottom, about 2.5 cm deep and about 7.5 cm × 7.5 cm square at the top. A funnel is then used to add 20 g (W_U) of a synthetic urine solution preparable by dissolving 2.0 g of KCl, 2.0 g of Na_2SO_4, 0.85 g of $NH_4H_2PO_4$, 0.15 g of $(NH_4)_2HPO_4$, 0.19 g of $CaCl_2$, and 0.23 g of $MgCl_2$ in 1 liter of distilled water to the center of the weighing boat. The time for the hydrogel to absorb all of the fluid, as indicated by the absence of pooled fluid, is recorded and noted as t_A. The Free Swell Rate then computes from

$$FSR = W_U/(W_H \times t_A)$$

Saline Flow Conductivity (SFC)

The test method for determining SFC is described in WO 95/262/9.

Vortex Time

50 ml of 0.9% by weight NaCl solution are measured into a 100 ml beaker. While the saline solution is being stirred with a magnetic stirrer at 600 rpm 2.00 g of hydrogel is poured in quickly in such a way that clumping is avoided. The time in seconds is taken for the vortex created by the stirring to close and for the surface of the saline solution to become flat.

Gel strength

The rheological studies to determine the gel strength were carried out on a CSL 100 controlled stress rheometer from Carrimed. All measurements are carried out at room temperature.

Sample preparation: The measurements are carried out on hydrogel particles of the sieve fraction 300-400 μm which had previously been preswelled for 1 hour in 0.9% by weight NaCl solution in a ratio of 1:60. To prepare the samples to be measured, the NaCl solution is initially charged to 100 ml beakers and the dry hydrogel particles are gradually added with (magnetic) stirring so that there is no clumping. The stirring bar is subsequently removed, and the beaker is sealed with a film and set aside for 1 hour in that state at room temperature for swelling. To ensure the same conditions prior to the measurement being carried out, this preparative method has to be complied with exactly, or the rheological measurement would be impaired and the measured results distorted.

Measurement procedure: The gel strength is determined using the Carrimed CS rheometer via the oscillation mode using a plate-plate geometry (diameter 6 cm). To avoid the slip effect, sandblasted plate systems are used for this purpose. The sample is placed on the baseplate and the ramp is slowly lifted to enable the gap to be closed slowly. The measuring gap measures 1 mm and has to be absolutely completely filled with sample material. Gel strength is the modulus of elasticity of the hydrogel preswollen as defined and is measured similarly to the modulus of elasticity in the linearly viscoelastic region of the sample, which is determined in a preliminary test on the same sample. To subsequently determine the gel strength, a torque sweep is carried out within the linearly viscoelastic region at a constant frequency (1 Hz) in the oscillation mode. Given elastic behavior, the measuring curve obtained is a straight line which quantifies the gel strength as a material constant of the elastic solid.

The reported measurements are number averages of 3 series of determinations.

The examples which follow illustrate the invention.

Examples

Inventive Example 1:

A 10 l capacity polyethylene vessel thoroughly insulated by foamed plastic material is charged with 3 600 g of deionized water and 1 400 g of acrylic acid, followed by 4.0 g of tetraallyloxyethane and 5.0 g of allyl methacrylate. The initiators, consisting of 2.2 g of 2,2'-azobisamidinopropane dihydrochloride (dissolved in 20 g of deionized water), 4 g of potassium peroxodisulfate (dissolved in 150 g of deionized water) and 0.4 g of ascorbic acid (dissolved in 20 g of deionized water) are successively added and stirred in at 4°C. The reaction solution is then left to stand without stirring. The ensuing polymerization, in the course of which the temperature rises up to about 90°C, produces a firm gel. This is subsequently subjected to mechanical comminution and adjusted to pH 6.0 with 50% by weight aqueous sodium hydroxide solution. The gel is then dried, ground and classified to a particle size distribution of 100 – 850 µm. 1 kg of this dried hydrogel is sprayed with a solution consisting of 60 g of demineralized water, 40 g of i-propanol and 1.0 g of ethylene glycol diglycidyl ether in a plowshare mixer and subsequently heat treated at 140°C for 60 minutes. The herein described product has the following properties:

CRC	=	28.4 g/g
AUL 0.7 psi	=	25.1 g/g
Gel strength	=	2 350 Pa
SFC	=	35×10^{-7} cm^3s/g

Inventive Example 2:

A 30 l capacity polyethylene vessel thoroughly insulated by foamed plastic material is charged with 14 340g of demineralized water and 42 g of sorbitol triallyl ether. 3 700 g of sodium bicarbonate are suspended in this initial charge and 5 990 g of acrylic acid are gradually added at a rate such that overfoaming of the reaction solution is avoided; the reaction solution cools down to about 3-5°C. The initiators, 6.0 g of 2,2'-azobisamidinopropane dihydrochloride (dissolved in 60 g of demineralized water), 12 g of potassium peroxodisulfate (dissolved in 450 g of demineralized water) and also 1.2 g of ascorbic acid (dissolved in 50 g of demineralized water) are successively added and thoroughly stirred in at 4°C. The reaction solution is then left to stand without stirring. The ensuing polymerization, in the course of which the temperature rises up to about 85°C, produces a gel. This gel is subsequently transferred into a kneader and adjusted to a pH of 6.2 by addition of 50% by weight aqueous sodium hydroxide solution. The comminuted

gel is then dried in an airstream at 170°C, ground and classified to a particle size distribution of 100 - 850 µm. 1 kg of this product is sprayed with a solution of 2 g of RETEN 204 LS (polyamidoamine-epichlorohydrin adduct from Hercules), 30 g of demineralized water and 30 g of 1,2-propanediol in a plowshare mixer and subsequently heat treated at 150°C for 60 minutes. The following properties were measured:

CRC	=	32.3 g/g
AUL 0.7 psi	=	26.4 g/g
Gel strength	=	1 975 Pa
SFC	=	25×10^{-7} cm^{3}s/g

Inventive Example 3:

A WERNER & PFLEIDERER laboratory kneader having a working capacity of 2 l is evacuated to 980 mbar absolute by means of a vacuum pump and a previously separately prepared monomer solution which has been cooled to about 25°C and inertized by passing nitrogen into it is sucked into the kneader. The monomer solution has the following composition: 825.5 g of deionized water, 431 g of acrylic acid, 335 g of NaOH 50%, 4.5 g of ethoxylated trimethylolpropane triacrylate (SR 9035 oligomer from SARTOMER) and 1.5 g of pentaerythritol triallyl ether (P-30 from Daiso). To improve the inertization, the kneader is evacuated and subsequently refilled with nitrogen. This operation is repeated three times. A solution of 1.2 g of sodium persulfate (dissolved in 6.8 g of deionized water) is then sucked in, followed after a further 30 seconds by a further solution consisting of 0.024 g of ascorbic acid dissolved in 4.8 g of deionized water. After a nitrogen purge a preheated jacket heating circuit on bypass at 75°C is switched over to the kneader jacket and the stirrer speed increased to 96 rpm. Following the onset of polymerization and the reaching of T_{max}, the jacket heating circuit is switched back to bypass, and the batch is supplementarily polymerized for 15 minutes without heating/cooling, subsequently cooled and discharged. The resultant gel particles are dried at above 100°C, ground and classified to a particle size distribution of 100 - 850 µm. 500 g of this product are sprayed with a solution of 2 g of 2-oxazolidinone, 25 g of deionized water and 10 g of 1,2-propanediol in a plowshare mixer and subsequently heat treated at 185°C for 70 minutes. The following properties were measured:

CRC	=	26.3 g/g
AUL 0.7 psi	=	23.8 g/g
Gel strength	=	2 680 Pa
SFC	=	50×10^{-7} cm^{3}s/g

Inventive Example 4:

1 000 g of the polymer of inventive example 1 were plowshare mixed for 15 minutes with 10 g of Sipernat D 17 (hydrophobic precipitated silica, commercial product of Degussa AG, average particle size 10 µm). The product thus coated has the following properties:

CRC	=	28.9 g/g
SFC	=	115×10^{-7} cm^3s/g
Vortex Time	=	80 s

Inventive Example 5:

1 000 g of the polymer of inventive example 1 were sprayed with 50 g of a solution consisting of 90 parts by weight of deionized water and 10 parts by weight of aluminum sulfate ($Al_2(SO_4)_3$) in a plowshare mixer and subsequently supplementarily mixed therein for 30 minutes. The product thus obtained has the following properties:

CRC	=	27.2 g/g
SFC	=	160×10^{-7} cm^3s/g
Free Swell Rate	=	0.25 g/gs

Inventive Example 6:

1 000 g of the polymer of inventive example 1 were plowshare mixed for 15 minutes with 8 g of Sipernat 22 (hydrophilic precipitated silica, commercial product of Degussa AG, average particle size 100 µm). The product thus coated has the following properties:

CRC	=	29.5 g/g
SFC	=	100×10^{-7} cm^3s/g
Free Swell Rate	=	0.56 g/gs

Inventive Example 7:

1 000 g of the polymer of inventive example 2 were plowshare mixed for 15 minutes with 10 g of Kieselsäure FK 320 (hydrophilic precipitated silica, commercial product of Degussa AG, average particle size 15 µm). The product thus coated has the following properties:

CRC	=	32.6 g/g
SFC	=	95×10^{-7} cm^3s/g
Vortex Time	=	58 s

Inventive Example 8:

1 000 g of the polymer of inventive example 2 were sprayed with a solution consisting of 40 g of deionized water, 20 g of Polymin G 100 solution and 0.5 g of SPAN 20 in a plowshare mixer and subsequently supplementarily mixed therein for 20 minutes. The product thus obtained has the following properties:

CRC	=	35.4 g/g
SFC	=	90×10^{-7} cm^3s/g
Vortex Time	=	45 s

Inventive Example 9:

1 000 g of the polymer of inventive example 3 were plowshare mixed for 15 minutes with 10 g of Sipernat D 17. The product thus coated has the following properties:

CRC	=	25.8 g/g
SFC	=	210×10^{-7} cm^3s/g
Vortex Time	=	105 s

Inventive Example 10:

1 000 g of the polymer of inventive example 3 were sprayed with a solution consisting of 50 g of deionized water, 10 g of polyvinylamine (K 88), 0.1 g of ethylene glycol diglycidyl ether and 0.5 g of SPAN 20 in a plowshare mixer and subsequently supplementarily mixed therein for 20 minutes. After heat treatment in a laboratory drying cabinet at 80°C for 1 hour, the product has the following properties:

CRC	=	25.6 g/g
SFC	=	330×10^{-7} cm^3s/g
Vortex Time	=	20 s

Comparative Example 1:

A 10 l capacity polyethylene vessel thoroughly insulated by foamed plastic material is charged with 3 600 g of deionized water and 1 400 g of acrylic acid, followed by 14 g of tetraallylammonium chloride. The initiators, consisting of 2.2 g of 2,2'-azobisamidinopropane dihydrochloride (dissolved in 20 g of deionized water), 4 g of potassium peroxodisulfate (dissolved in 150 g of deionized water) and 0.4 g of ascorbic acid (dissolved in 20 g of deionized water) are successively added and stirred in at 4°C. The reaction solution is then left to stand without stirring. The ensuing polymerization, in the course of which the temperature rises up to about 90°C, produces a firm gel. This is subsequently subjected to mechanical comminution and adjusted to pH 6.0 with 50% by weight aqueous sodium hydroxide solution. The gel is then dried, ground and classified to a particle size distribution of 100 - 850 µm. 1 kg of this dried hydrogel is sprayed with a solution consisting of 40 g of demineralized water, 40 g of i-propanol and 0.5 g of ethylene glycol diglycidyl ether in a plowshare mixer and subsequently heat treated at 140°C for 60 minutes. The herein described product has the following properties:

CRC	=	36.2 g/g
AUL 0.7 psi	=	25.9 g/g
Gel strength	=	1 580 Pa
SFC	=	8×10^{-7} cm^{3}s/g

Comparative Example 2:

A WERNER & PFLEIDERER laboratory kneader having a working capacity of 2 l is evacuated to 980 mbar absolute by means of a vacuum pump and a previously separately prepared monomer solution which has been cooled to about 25°C and inertized by passing nitrogen into it is sucked into the kneader. The monomer solution has the following composition: 825.5 g of deionized water, 431 g of acrylic acid, 335 g of NaOH 50%, 3.0 g of methylenebisacrylamide. To improve the inertization, the kneader is evacuated and subsequently refilled with nitrogen. This operation is repeated three times. A solution of 1.2 g of sodium persulfate (dissolved in 6.8 g of deionized water) is then sucked in, followed after a further 30 seconds by a further solution consisting of 0.024 g of ascorbic acid dissolved in 4.8 g of deionized water. After a nitrogen purge a preheated jacket heating circuit on bypass at 75°C is switched over to the kneader jacket and the stirrer speed increased to 96 rpm. Following the onset of polymerization and the reaching of T_{max}, the jacket heating circuit is switched back to bypass, and the batch is supplementarily polymerized for 15 minutes without heating/cooling, subsequently cooled and discharged. The resultant gel particles are dried at above 100°C, ground and classified to a particle size distribution of 100 - 850 µm. The following properties were measured:

CRC	=	29.4 g/g
AUL 0.7 psi	=	15.8 g/g
Gel strength	=	1 920 Pa
SFC	=	5×10^{-7} cm^{3}s/g

Comparative Example 3:

1 000 g of the polymer of comparative example 1 were plowshare mixed for 15 minutes with 10 g of Sipernat D 17 (hydrophobic precipitated silica, commercial product of Degussa AG, average particle size 10 µm). The product thus coated has the following properties:

CRC	=	35.8 g/g
SFC	=	11×10^{-7} cm^{3}s/g
Vortex Time	=	85 s

Comparative Example 4:

1 000 g of the polymer of comparative example 1 were sprayed with 50 g of a solution consisting of 90 parts by weight of deionized water and 10 parts by weight of aluminum sulfate ($Al_2(SO_4)_3$) in a plowshare mixer and subsequently supplementarily mixed therein for 30 minutes. The product thus obtained has the following properties:

CRC	=	34.6 g/g
SFC	=	9×10^{-7} cm^{3}s/g
Free Swell Rate	=	0.48 g/gs

Comparative Example 5:

1 000 g of the polymer of comparative example 2 were plowshare mixed for 15 minutes with 10 g of Sipernat D 17. The product thus coated has the following properties:

CRC	=	29.7 g/g
SFC	=	6×10^{-7} cm^{3}s/g
Vortex Time	=	78 s

Comparative Example 6:

1 000 g of the polymer of comparative example 2 were sprayed with a solution consisting of 50 g of deionized water, 10 g of polyvinylamine (K 88), 0.1 g of ethylene glycol diglycidyl ether and 0.5 g of SPAN 20 in a plowshare mixer and subsequently supplementarily mixed therein for 20 minutes. After heat treatment in a laboratory drying cabinet at 80°C for 1 hour, the product has the following properties:

CRC	=	27.8 g/g
SFC	=	15×10^{-7} cm^{3}s/g
Vortex Time	=	35 s

Comparative Example 7:

A 30 l capacity polyethylene vessel thoroughly insulated by foamed plastic material is charged with 14 340 g of demineralized water and 42 g of sorbitol triallyl ether. 3 700 g of sodium bicarbonate are suspended in this initial charge and 5 990 g of acrylic acid are gradually added at a rate such that overfoaming of the reaction solution is avoided; the reaction solution cools down to about 3-5°C. The initiators, 6.0 g of 2,2'-azobisamidinopropane dihydrochloride (dissolved in 60 g of demineralized water), 12 g of potassium peroxodisulfate (dissolved in 450 g of demineralized water) and also 1.2 g of ascorbic acid (dissolved in 50 g of demineralized water) are successively added and thoroughly stirred in at 4°C. The reaction solution is then left to stand without stirring. The ensuing polymerization, in the course of which the temperature rises up to about 85°C, produces a gel. This gel is subsequently transferred into a kneader and adjusted to a pH of

6.2 by addition of 50% by weight aqueous sodium hydroxide solution. The comminuted gel is then dried in an airstream at 170°C, ground and classified to a particle size distribution of 100 - 850 μm and homogeneously mixed with 1.0% by weight of Aerosil 200 (pyrogenic silica, commercial product of Degussa AG, average primary particle size 12 nm). 1 kg of this product is sprayed with a solution of 2 g of RETEN 204 LS (polyamidoamine-epichlorohydrin adduct from Hercules), 30 g of demineralized water and 30 g of 1,2-propanediol in a plowshare mixer and subsequently heat treated at 150°C for 60 minutes. The following properties were measured:

CRC	=	31.8 g/g
SFC	=	25×10^{-7} cm^{3}s/g
Vortex Time	=	65 s

Comparative Example 8:

A 30 l capacity polyethylene vessel thoroughly insulated by foamed plastic material is charged with 14 340 g of demineralized water and 42 g of sorbitol triallyl ether. 3 700 g of sodium bicarbonate are suspended in this initial charge and 5 990 g of acrylic acid are gradually added at a rate such that overfoaming of the reaction solution is avoided; the reaction solution cools down to about 3-5°C. The initiators, 6.0 g of 2,2'-azobisamidinopropane dihydrochloride (dissolved in 60 g of demineralized water), 12 g of potassium peroxodisulfate (dissolved in 450 g of demineralized water) and also 1.2 g of ascorbic acid (dissolved in 50 g of demineralized water) are successively added and thoroughly stirred in at 4°C. The reaction solution is then left to stand without stirring. The ensuing polymerization, in the course of which the temperature rises up to about 85°C, produces a gel. This gel is subsequently transferred into a kneader and adjusted to a pH of 6.2 by addition of 50% by weight aqueous sodium hydroxide solution. The comminuted gel is then dried in an airstream at 170°C, ground and classified to a particle size distribution of 100 - 850 μm. 1 kg of this product is sprayed with a solution of 2 g of RETEN 204 LS (polyamidoamine-epichlorohydrin adduct from Hercules), 5 g of aluminum sulfate $Al_2(SO_4)_3$, 30 g of demineralized water and 30 g of 1,2-propanediol in a plowshare mixer and subsequently heat treated at 150°C for 60 minutes. The following properties were measured:

CRC	=	31.5 g/g
SFC	=	24×10^{-7} cm^{3}s/g
Vortex Time	=	73 s

As enclosed to IPER

We claim:-

1. Water-insoluble water-swellable hydrogels coated with steric or electrostatic spacers, characterized by the following pre-coating features:

   - Absorbency Under Load (AUL) (0.7 psi) of at least 20 g/g,
   - Gel strength of at least 1 600 Pa, wherein the steric or cationic spacers are applied to the surface of the hydrogel in an amount of from 0.05 to 5% by weight, based on the total weight of the coated hydrogels.

2. Hydrogels as claimed in claim 1, characterized by the following post-coating features:

   - Centrifuge Retention Capacity (CRC) of at least 24 g/g,
   - Saline Flow Conductivity (SFC) of at least 30×10^{-7} cm^3s/g and
   - Free Swell Rte (FSR) of at least 0.15 g/g and/or Vortex Time of not more than 160 s.

3. Hydrogels as claimed in claim 1 or 2, wherein the steric spacers are selected from bentonites, zeolites, active carbons and silicas.

4. Hydrogels as claimed in claim 1 or 2, wherein the electrostatic spacers are cationic polymers.

5. A water-absorbent composition containing water-insoluble water-swellable hydrogels as claimed in any of claims 1 to 4.

6. A water-absorbent composition as claimed in claim 5, wherein the water-swellable hydrogels are embedded as particles in a polymer fiber matrix or an open-celled polymer foam, fixed on a sheetlike base material or present as particles in chambers formed from a base material.

7. The process for producing water-absorbent compositions as claimed in claim 6 by

   - preparing the water-swellable hydrogels,

- coating the hydrogels with a steric or electrostatic spacer and
- introducing the hydrogels into a polymer fiber matrix or an open-celled polymer foam or into chambers formed from a base material or fixing on a sheetlike base material.

8. The use of water-absorbent compositions as claimed in either of claims 5 and 6 for producing hygiene articles or other articles for absorbing aqueous fluids.

9. Hygiene articles containing a water-absorbent composition as claimed in either of claims 5 and 6 between a liquid-pervious topsheet and a liquid-impervious backsheet.

10. Hygiene articles as claimed in claim 9 in the form of diapers, sanitary napkins and incontinence products.

11. The method for improving the performance profile of water-absorbent compositions by enhancing the permeability, capacity and swell rate of the water-absorbent compositions by use of water-insoluble water-swellable hydrogels as defined in any of claims 1 to 4.

12. The method for determining water-absorbent compositions possessing high permeability, capacity and swell rate by measuring the Absorbency Under Load (AUL) and the gel strength of uncoated hydrogels and determining the Centrifuge Retention Capacity (CRC), Saline Flow Conductivity (SFC) and Free Swell Rate (FSR) of the coated hydrogels for given water-absorbent compositions and determining the water-absorbent compositions for which the hydrogels exhibit the property spectrum mentioned in claim 1 or 2.

13. The use of water-insoluble water-swellable hydrogels as defined in any of claims 1 to 4 in hygiene articles or other articles for absorbing aqueous fluids to enhance the permeability, capacity and swell rate.